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SUMMARY

The stability of alcohol solutions of norbornenyl capped PMR-polyimide resins (both PMR-15 and PMR-II) has been monitored during storage at ambient and subambient (5°C and -18°C) temperatures. Chemical changes during storage were determined spectroscopically using nuclear magnetic resonance. Resin processability and cured resin quality were determined by fabrication of unidirectional, graphite fiber composites using aged solutions and testing of selected composite properties. PMR-15 solutions exhibit nominally two weeks of useful life and PMR-II solutions exhibit nominally two days of useful life at ambient conditions. The limiting factor is precipitation of imide reaction products from the monomer solutions. Both solutions exhibit substantially longer useful lifetimes in subambient storage. PMR-15 shows no precipitation after several months storage at subambient temperatures. PMR-II solutions do exhibit precipitates after extended subambient storage (nominally three months at -18°C), however, the precipitates formed under these conditions can be redissolved. The chemical implications of these observations are discussed.

INTRODUCTION

Solutions of polymer precursors have, inherently, a finite storage life. The shelf life depends on many factors such as degree of reactivity of the material, concentration of the reactants, storage conditions (time and temperature) and other factors which affect the initiation or rate of chemical reactions. The situation is further complicated by the fact that reactions occurring during storage are not necessarily the same reactions that are expected during processing of the polymer. This is particularly the case for polymer systems which have been tailored to cure at elevated temperatures. The monomer solutions employed in this study were precursors for two versions of the high temperature resistant, addition-type polyimide resin system (designated PMR for polymerization of monomer reactants) developed at the Lewis Research Center (Refs. 1, 2, 3). Table 1 shows the monomers used for both types of PMR solutions. The first generation system (PMR-15) uses an alcohol solution of three monomer reactants: the reactive end cap, NE (monomethylester of 5-norbornene-2, 3-dicarboxylic acid); the diamine, MDA (4, 4'-methylenedianiline); and the diacid-diester, BTDE (dimethylester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid). The second

generation system (PMR-II) uses an alcohol solution of three analogous reactants: the same reactive end cap, NE; the diamine, PPDA (p-phenylenediamine); and the diacid-diester, HFDE (dimethylester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid)). The principal solvent of interest for the PMR solutions is methanol, however, alternate solvent systems were considered in this study.

The solution stability of PMR resin solutions and related polymer materials has been qualitatively assessed in prior studies (Ref. 1), but has not been analyzed in detail. The effect of specific ester impurities in PMR polyimide resin has been studied (Ref. 4).

The purpose of this study was to investigate the solution stability of selected PMR-polyimide monomer solutions in typical storage conditions, to determine the chemical factors which limit the solution shelf life, and to identify the effect of solution aging on polymer processing and on selected polymer/graphite fiber composite properties.

EXPERIMENTAL

Reagents. - The monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE), the 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), the 4,4'-methylene-dianiline (MDA), and the p-phenylenediamine (PPDA) were the highest quality commercially available materials and were used without further purification. The diethylester of 4,4'-(hexafluoroisopropylidene)-bis(phthalic acid) (HFDE, R = Et) was purchased as one component in a commercial solution (Dupont NRO5OX) of HFDE, R = Et and PPDA in ethanol. The HFDE, R = Me was prepared as described in Ref. 3. Anhydrous methanol and ethanol were employed.

The PMR-15 monomer solutions were prepared as described in Ref. 5. The solutions were formulated at fifty percent by weight in methanol in the proportion: n moles of BTDE/(n+1) moles of MDA/2 moles of NE, where n = 2.08. The PMR-II monomer solutions were prepared as described in Ref. 3 in three different solvent systems. All were formulated at fifty percent by weight in the proportion: n moles of HFDE/(n+1) moles of PPDA/2 moles of NE, where n = 1.67. Solutions containing HFDE, R = Et were prepared in ethanol and in 50/50 mixtures of methanol/ethanol using the NRO5OX solutions. Solutions containing HFDE, R = Me were prepared in methanol as described in Ref. 6.

The model compound, p-amino-N-phenylnadimide (m. p. 234-234.5° C, theory: C = 70.85%, H = 5.55%, N = 11.37%), was prepared by aluminum amalgam reduction of p-nitro-N-phenylnadimide. The p-nitro-N-phenylnadimide was prepared from nadic anhydride and p-nitroaniline in acidified 95% ethanol or acetic anhydride at their respective reflux temperatures.

Instrumental measurements. - Nuclear magnetic resonance measurements were obtained on a commercial, 60 MHz, continuous wave instrument. Data were referenced to internal tetramethylsilane. Sample solutions were diluted approximately four fold with deuterio-chloroform for the measurements. Solutions of solid precipitates were dissolved in perdeutero-dimethylsulfoxide for analysis. All data were electronically integrated. Infrared spectral measurements were made on a commercial, double beam spectrometer. Samples of precipitates and model compounds were examined as solids in potassium bromide pellets.

Composite fabrication and testing. - Prepreg tapes were made by drum winding and impregnating HTS graphite fiber with PMR-15 monomer solutions to yield prepreg containing 54.5 percent fiber by weight. The prepreg was air dried for 1 hr at ambient temperatures and 1 hr at 49° C. The prepreg was cut into 7.6x20.3 cm plies and stacked unidirectionally, 8 plies thick. These stacks were staged at 121° C for 3 hrs under 0.1 psi load. The composites were cured in a matched metal die preheated to 232° C. Following a dwell time of 10 minutes, 500 psi pressure was applied and the temperature increased to 316° C at 5.5° C/min. Pressure and temperature were maintained for 60 minutes. Prior to test specimen preparation, all laminates were inspected using ultrasonic C scan. Flexural strength tests and interlaminar shear strength tests were performed at ambient temperature and at 316° C as described in Ref. 6.

RESULTS AND DISCUSSION

PMR-15 solutions. - Visual observations during extended aging of PMR-15 monomer solutions at ambient, 5° C, and -18° C are summarized in Table 2. The most revealing observation noted in Table 2 is the formation of a precipitate at ambient conditions after about 17 days. The nature of this precipitate will be discussed later. Subambient storage greatly increases the shelf life of the PMR-15 solutions as indicated by the lack of precipitate formation after more than 6 months of storage at the lower temperatures. Increased color in the solutions (a deeper amber brown) may be due to slight oxidation of the aromatic amine (MDA) or to increased protonation of the amine as discussed below. The appearance of two liquid phases during storage is unique to the -18° C sample. This sample exhibited a very darkly colored, viscous layer below a very lightly colored, methanol rich layer. The layers did not intermix rapidly when warmed to room temperature but could be homogeneously dispersed with mechanical stirring; the separation recurred upon cooling to the storage temperature. Because the liquid phases could be easily intermixed, this phenomenon was not considered to be a direct limitation of storage life at this condition.

Spectral analysis of the monomer solutions during storage and of the isolated precipitate permit greater insight into the reactions occurring during solution aging. Proton magnetic resonance spectra of the solution aged at ambient conditions are shown in Fig. 1. The three spectral features shown in the figure are: resonances due to the bridgehead protons (~ 1.3 ppm) and olefinic protons (~ 6.2 ppm) of NE; resonances due to the phenyl protons of MDA (~ 6.5 – 7.3 ppm); and the resonances due to the phenyl protons of BTDE (above 7.5 ppm). These spectral features are conveniently separated in all the monomer solutions and, for the fresh solution (time zero), are characteristic of a simple mixture of the unreacted monomers. However, significant changes are evident in the spectrum of the aged solution at the time of initial precipitation. First, the NE bridgehead resonance is diminished and a new resonance occurs near 1.7 ppm. This new peak is characteristic of the bridgehead protons of nadimide compounds. Second, the pseudoquartet of resonances due to MDA appears to be diminished with a new peak (or peaks) overlayed near 6.9 ppm. The interpretation of this spectral feature is not complete, however, it is apparent that, in the aged solution, there is a strong interaction of NE and MDA. Infrared spectra of the precipitate confirm the presence of imidized material, but the precipitate, as isolated, appeared to be a mixture of materials and, hence, elemental analysis was not performed. Based on the spectral evidence for the presence of nadimide, and by analogy with the PMR-II data discussed below, it is inferred that the initial precipitate formed during ambient aging is the imide formed from one mole of NE and one mole of MDA. The occurrence of this reaction at ambient temperatures may seem exceptional since the imidization reaction in PMR-15 resin is typically reported (Ref. 4) in the temperature range 120° to 200° C. However, to a reasonable approximation, the formation of measurable amounts of imide at 23° C is consistent with the rate data and activation energy for imidization previously discussed (Refs. 4, 7). The observation of nadimide and not a product involving BTDE, is consistent with the greater acidity, and correspondingly greater reactivity, of the NE relative to the BTDE. The observation (discussed below) that the formation of nadimide is greatly retarded during lower temperature storage supports this kinetic argument.

Proton magnetic resonance spectra of the monomer solution stored at -18° C are shown in Fig. 2. The solution stored at 5° C exhibited a similar progression of spectra but advanced at a more rapid rate. The major difference in these spectra relative to the ambient storage data of Fig. 1 is the minimal change in the NE resonance peaks. At 5° C there was a slight indication of the nadimide resonance at 1.7 ppm after about 6 months of solution storage, but effectively, the reaction involving NE and MDA and the resultant precipitate formation was not observed during storage of PMR-15 solutions at 5° C and -18° C. A second spectral feature that is characteristic of the solutions in the low temperature storage is the collapse of the pseudoquartet due to the phenyl resonances of MDA and the concurrent broadening and splitting of the BTDE phenyl peaks. These spectral changes suggest

that BTDE and MDA are interacting in the solution. The collapse of the MDA resonances is probably due simply to successively increased protonation of the amine. By analogy with the PMR-II data discussed below, it is inferred that salt formation (solution ion pairing) is occurring between BTDE and MDA. This provides a reasonable explanation for the liquid/liquid phase separation observed during -18°C storage. It appears that, after extended storage at -18°C (nominally 1 month) the ion pairing is of adequate extent and ionic strength to partially exclude the more weakly interacting solvent. Spectral observations of the two liquid phases support this model. Magnetic resonance spectra of the viscous lower phase showed a composition rich in MDA and BTDE, while the spectrum of the lighter, methanol phase showed predominantly NE and MDA. It appears that there is no formation of amides or other oligomers in the viscous phase because solubility is maintained and, upon dilution, the spectral data are consistent with a monomer solution. As observed above, the liquid phases could be intermixed and, as a homogeneous solution, showed no significant changes in stoichiometry based on the spectral observations.

The potential formation of ester impurities in the aged PMR-15 solutions was investigated because the deleterious effect of such impurities (higher esters of BTDE) has been discussed (Ref. 4). Figure 3 shows magnetic resonance spectra of the spectral region in which methyl ester resonance peaks occur. At time zero, the spectrum appears to be a simple mixture of the monomers. Approximate integration and subsequent normalization of the resonance peaks shows that the components are present in the appropriate molar ratios and that there are, as theoretically expected, two methyl ester groups per BTDE and one methyl ester group per NE. During storage at ambient conditions, no change of significance occurred up to the time of precipitation (the change in the ester content of NE discussed below was not monitored during the brief time of ambient exposure). However, during low temperature storage, the BTDE ester peaks shift to smaller values of δ . This shift corresponds to the BTDE/MDA interaction discussed above. The integral data show no significant change in BTDE ester group content. Thus it appears that no higher esters of BTDE are forming during extended storage (more than 4 months) at subambient temperatures. Integration and normalization of the NE ester peak does show some increase in peak area with time. The system appears to equilibrate at nominally 1.3 ester groups per NE compared to 1.0 for the theoretical compositions (thus, 30 percent of NE is diester). The effect of this diester impurity has not been investigated.

Graphite fiber prepreg and unidirectional composite samples were fabricated from the aged solutions. Samples were prepared after 17 days storage at ambient conditions (just prior to precipitate formation) and at 1 month intervals for solutions stored at subambient temperatures. Observations were referenced to a control sample prepared with a fresh resin solution. Qualitatively, slight variations

were observed in processing the solutions aged at subambient temperatures. Solutions aged for 1 month at either 5°C or -18°C exhibited slightly diminished flow during processing. Solutions aged 4 months at these temperatures exhibited poorer fiber wetting during prepreg preparation. Both of these observations are consistent with an increase in viscosity of the monomer solutions. These slight variations in processing were not severe enough to significantly diminish the quality of the composite panels. Figure 4 shows the negligible variation in flexural strength and interlaminar shear strength (both tested at ambient temperature and 316°C) as a function of monomer solution storage time. Only after 4 months storage does it appear that the mechanical properties may be reduced. The flexural and shear strengths exhibited by all the test panels were typical of high quality laminates. Inspection by ultrasonic C-scan showed the panels to be of acceptable quality.

PMR-II solutions. - The approximate times to precipitation for selected PMR-II monomer solutions are summarized in Table 3. It should be noted that detection of initial precipitation in these solutions is difficult because of the very dark color (deep purple, nearly opaque) of the solutions and the fact that small volumes of precipitate are formed at low temperatures. The most apparent aspect of these data is the exceptionally short times to precipitation (3 days or less) for the PMR-II solutions stored at ambient conditions. Two more predictable trends in the data are also evident. First, subambient storage significantly increased the time to precipitation of the monomer solutions (nominally 1 month at 5°C and 2 months at -18°C). Second, there was a slight improvement in the time to precipitation in the methanol solutions relative to the ethanol solutions. This reflects the slightly greater solubility of the PMR monomers in methanol.

The precipitates were analyzed (melting point, elemental composition (Table 4), infrared and proton magnetic resonance spectroscopy (Fig. 5)) and it was found that the precipitate formed at ambient conditions was not the same as that formed at 5°C and -18°C . At ambient conditions the precipitate was the imide formed by one mole of NE and one mole of PPDA. The analytical data are all consistent with this structure and it was confirmed by direct comparison with p-amino-N-phenylnadimide prepared and characterized for this study. As discussed earlier, this parallels the chemistry occurring in the PMR-15 solutions. The more rapid reaction in the PMR-II monomer solution is consistent with the greater basicity of PPDA relative to MDA and the resultant increased reactivity towards acids. The PPDA nadimide is probably less soluble than the MDA analog and this would contribute to more rapid precipitation also. The precipitate formed at subambient temperatures had the approximate composition of a 1:2 salt of HFDE and PPDA. This precipitate melted at moderate temperature (119° to 122°C) with evolution of volatiles (apparent amide and imide formation). The precipitate dissolves in alcohol with mechanical stirring and/or slight warming,

however, even gentle application of heat may lead to precipitation of the insoluble nadimide. Because the low temperature precipitate can be redissolved, the monomer solution can still be processed. Thus, the time of formation of this precipitate need not be used as an indication of the limit of shelf life for the PMR-II monomer solutions.

Proton magnetic resonance spectra of the PMR-II solutions were not as definitive as those for PMR-15. In particular, there was no spectral indication of the nadimide prior to precipitation. This is probably due to the limited solubility of the PPDA nadimide. Also, the PPDA phenyl resonances (near 6.8 ppm) were broad and showed little change even during extended storage at subambient temperatures. This is probably related to the greater basicity of the PPDA which would result in increased extent of protonation of the amine groups and a broadening of the coupled phenyl protons even at ambient conditions. The phenyl proton resonances of HFDE (near 7.6 ppm) did show some discernable changes during solution storage at low temperatures which are consistent with the salt formation discussed above. Figure 5 compares the spectral region in which phenyl and olefinic magnetic resonance peaks occur for a fresh PMR-II solution and the two precipitates isolated from the aged PMR-II solutions. The fresh solution data are analogous to the PMR-15 spectra except for the broadness of the PPDA resonance. The spectrum of the ambient temperature precipitate exhibits peaks due only to the diamine and the nadic group. The integral data for this spectrum are consistent with the composition of the precipitate discussed above. The spectrum of the low temperature precipitate shows no NE resonance and the integral data are consistent with the HFDE/PPDA salt composition discussed above.

The methyl ester region of the PMR-II spectra exhibited the same trends previously discussed for the PMR-15 solutions except that no shift of the HFDE ester resonance was observed during storage. The integral data showed no significant increase in ester content of HFDE during extended storage. Thus, it appears that higher esters of HFDE are not forming during storage at 5° and -18° C. The NE ester content did increase during the first 8 hours of storage at ambient conditions, and all the PMR-II solutions appeared to equilibrate at nominally 1.3 ester groups per NE as did the PMR-15 solutions.

Composite samples were not prepared from the aged PMR-II solutions.

SUMMARY OF RESULTS

The stability of PMR-15 and PMR-II monomer solutions was studied at three temperatures. It was determined that:

(1) PMR monomer solutions exhibit finite shelf life at ambient conditions (nominally 2 weeks for PMR-15 and 2 days for PMR-II).

(2) The limiting factor for both PMR solutions in ambient storage is formation of insoluble nadimide precipitates.

(3) Storage of PMR monomer solutions at 5° and -18° C significantly increases shelf life of the solutions.

(4) Formation of salts of the diamine and the diacid/diester monomers during subambient storage leads to liquid/liquid phase separation in the PMR-15 solutions (-18° C) and to precipitation in the PMR-II solutions. These materials can still be processed with care.

(5) Composite panels prepared from aged PMR-15 solutions (17 days at ambient and up to 4 months at 5° and -18° C) exhibit properties typical of high quality panels. Slight decreases in resin flow and fiber wetting were the only variations noted in processing the aged solutions in this study.

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TABLE 1. - MONOMERS USED FOR PMR-POLYIMIDE SOLUTIONS

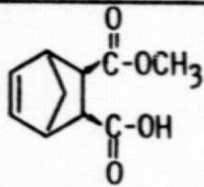
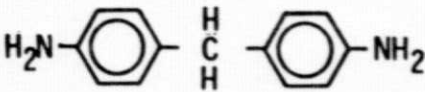
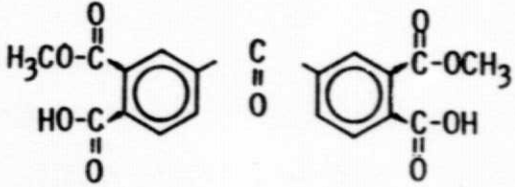
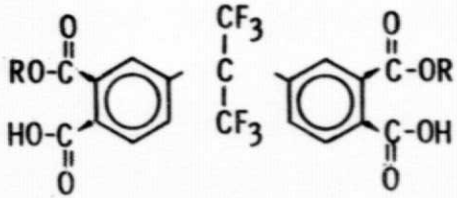
STRUCTURE	NAME	ABBREVIATION
	MONOMETHYLESTER OF 5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	4,4'-METHYLENEDIANILINE	MDA
	DIMETHYLESTER OF 3,3',4,4'-BENZOPHENONETETRACARBOXYLIC ACID	BTDE
	p-PHENYLENEDIAMINE	PPDA
	DIESTER OF 4,4'-(HEXAFLUOROISOPROPYLIDENE)-BIS (PHTHALIC ACID) R = METHYL, ETHYL	HFDE

TABLE 2. - OBSERVATIONS DURING PMR-15 MONOMER SOLUTION AGING

	Storage temperature		
	Ambient	5° C	-18° C
Solution appearance	Color darkened	Color darkened	Separated into two liquid phases
Precipitate formed	~ 17 days	none (after ~6 months)	none (after ~6 months)

TABLE 3. - STABILITY OF PMR-II SOLUTIONS
(Approximate time to precipitation, days,)

Solvent	Storage temperature		
	Ambient	5° C	-18° C
Ethanol	2	10	60
Ethanol/Methanol	3	34	79
Methanol	3	33	79

TABLE 4. - ANALYTICAL DATA FOR PMR-II PRECIPITATES

Precipitation condition	Melting point, °C	Observed composition, %
Ambient	234	C = 69.71 H = 5.51 N = 11.15 (D = 13.59)
Subambient	119-122 (With gas evolution)	C = 54.74 H = 4.75 N = 6.97 (D = 17.24)

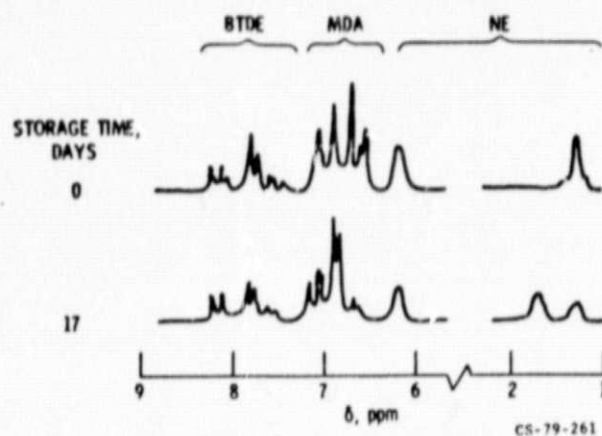


Figure 1. - Proton magnetic resonance spectra of PMR-15 monomer solutions (ambient storage).

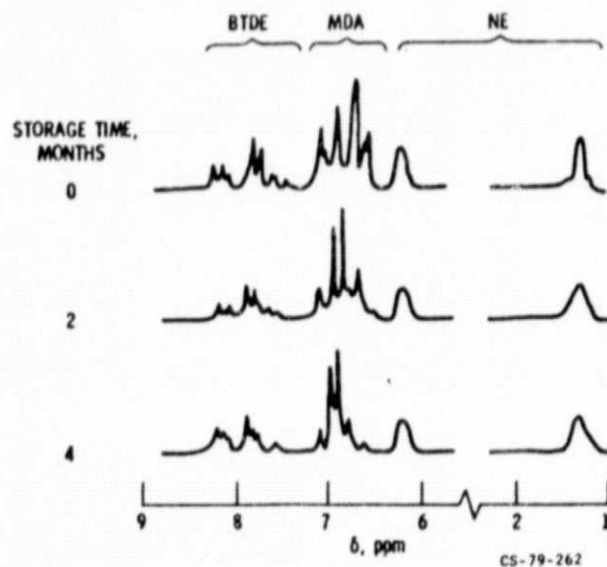


Figure 2. - Proton magnetic resonance spectra of PMR-15 monomer solutions (-18°C storage).

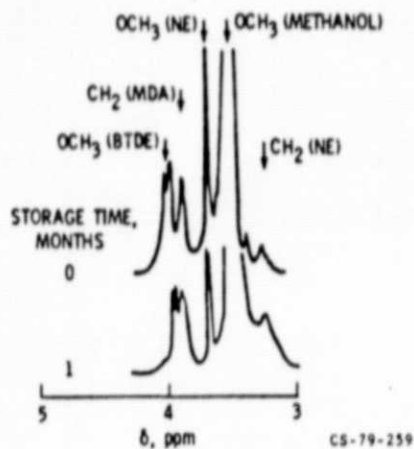


Figure 3. - Methylester region of proton magnetic resonance spectra of PMR-15 (-18°C storage).

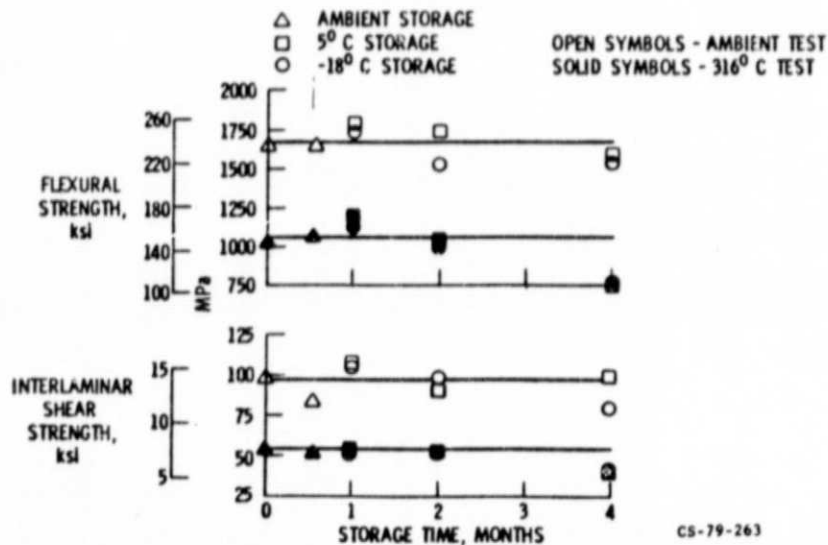


Figure 4. - Variations in flexural strength and interlaminar shear strength with monomer solution storage.

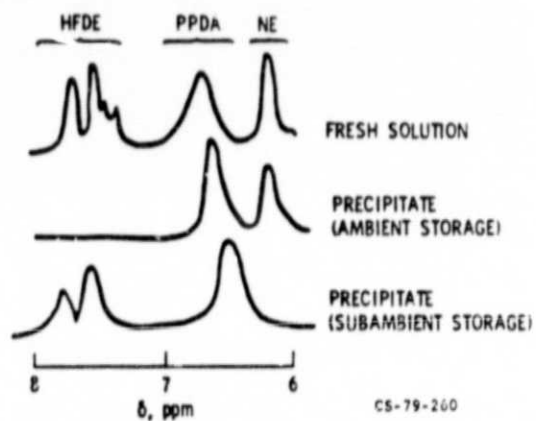


Figure 5. - Proton magnetic resonance spectra of PMR-II monomer solution and the precipitates formed during storage.